Raman spectroscopy

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Raman spectroscopy is a spectroscopic technique used in condensed matter physics and chemistry to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. Phonons or other excitations in the system are absorbed or emitted by the laser light, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system. Infrared spectroscopy yields similar, but complementary information.

Typically, a sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and sent through a monochromator. Wavelengths close to the laser line (due to elastic Rayleigh scattering) are filtered out and those in a certain spectral window away from the laser line are dispersed onto a detector.

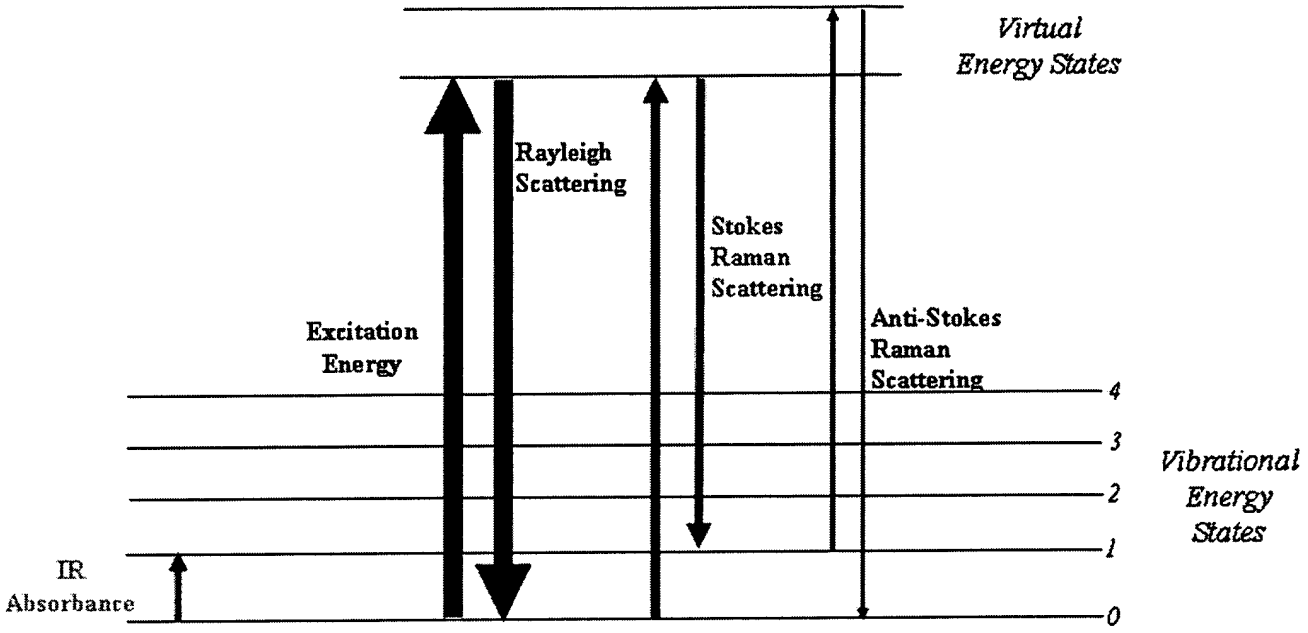
Spontaneous Raman scattering is typically very weak, and as a result the main difficulty of Raman spectroscopy is separating the weak inelastically scattered light from the intense Rayleigh scattered laser light. Raman spectrometers typically use holographic diffraction gratings and multiple dispersion stages to achieve a high degree of laser rejection. A photon-counting photomultiplier tube (PMT) or, more commonly, a CCD camera is used to detect the Raman scattered light. In the past, PMT were the detectors of choice for dispersive Raman setups, which resulted in long acquisition times. However, the recent uses of CCD detectors have made dispersive Raman spectral acquisition much more rapid.

Raman spectroscopy has a stimulated version, analogous to stimulated emission, called stimulated Raman scattering.

Contents

Basic theory

The Raman effect occurs when light impinges upon a molecule and interacts with the electron cloud of the bonds of that molecule. A molecular polarizability change, or amount of deformation of the electron cloud, with respect to the vibrational coordinate is required for the molecule to exhibit the Raman effect. The amount of the polarizability change will determine the intensity, whereas the Raman shift is equal to the vibrational level that is involved. The incident photon (light quantum), excites one of the electrons into a virtual state. For the spontaneous Raman effect, the molecule will be excited from the ground state to a virtual energy state, and relax into a vibrational excited state, and which generates Stokes Raman scattering. If the molecule was already in an elevated vibrational energy state, the Raman scattering is then called anti-Stokes Raman scattering.



Applications

Raman spectroscopy is commonly used in chemistry, since vibrational information is very specific for the chemical bonds in molecules. It therefore provides a fingerprint by which the molecule can be identified. The fingerprint region of organic molecules is in the range 500-2000 cm^{-1}. Another way that the technique is used is to study changes in chemical bonding, e.g. when a substrate is added to an enzyme.

Raman gas analyzers have many practical applications, for instance they are used in medicine for real-time monitoring of anaesthetic and respiratory gas mixtures during surgery.

In solid state physics, spontaneous Raman spectroscopy is used to, among other things, characterize materials, measure temperature, and find the crystallographic orientation of a sample.

As with single molecules, a given solid material has characteristic phonon modes that can help an experimenter identify it. In addition, Raman spectroscopy can be used to observe other low frequency excitations of the solid, such as plasmons, magnons, and superconducting gap excitations.

The spontaneous Raman signal gives information on the population of a given phonon mode in the ratio between the Stokes (downshifted) intensity and anti-Stokes (upshifted) intensity.

Raman scattering by an anisotropic crystal gives information on the crystal orientation. The polarization of the Raman scattered light with respect to the crystal and the polarization of the laser light can be used to find the orientation of the crystal, if the crystal structure (specifically, its point group) is known.

Raman active fibers, such as aramid and carbon, have vibrational modes that show a shift in Raman frequency with applied stress. Polypropylene fibers also exhibit similar shifts.

The radial breathing mode is a commonly used technique to evaluate the diameter of carbon nanotubes.

Spatially Offset Raman Spectroscopy (SORS), which is less sensitive to surface layers than conventional Raman, can be used to discover counterfeit drugs without opening their internal packaging, and for non-invasive monitoring of biological tissue [1][2].

Raman microspectroscopy

Raman spectroscopy offers several advantages for microscopic analysis. Since it is a scattering technique, specimens do not need to be fixed or sectioned. Raman spectra can be collected from a very small volume (< 1μm in diameter); these spectra allow the identification of species present in that volume. Water does not interfere very strongly. Thus, Raman spectroscopy is suitable for the microscopic examination of minerals, materials such as polymers and ceramics, cells and proteins. A Raman microscope begins with a standard optical microscope, and adds an excitation laser, a monochromator, and a sensitive detector (such as a charge-coupled device (CCD) or photomultiplier tube (PMT)). FT-Raman has also been used with microscopes.

In *direct imaging*, the whole field of view is examined for scattering over a small range of wavenumbers (Raman shifts). For instance, a wavenumber characteristic for cholesterol could be used to record the distribution of cholesterol within a cell culture.

The other approach is *hyperspectral imaging*, in which thousands of Raman spectra are acquired from all over the field of view. The data can then be used to generate images showing the location and amount of different components. Taking the cell culture example, a hyperspectral image could show the distribution of cholesterol, as well as proteins, nucleic acids, and fatty acids. Sophisticated signal- and image-processing techniques can be used to ignore the presence of water, culture media, buffers, and other interferents.

Raman microscopy, and in particular confocal microscopy, has very high spatial resolution. For example, the lateral and depth resolutions were 250 nm and 1.7 μm, respectively, using a confocal Raman microspectrometer with the 632.8 nm line from a He-Ne laser with a pinhole of 100 μm diameter.

Since the objective lenses of microscopes focuses the laser beam to several microns in diameter, the resulting photon flux is much higher than achieved in conventional Raman setups. This has the added benefit of enhanced fluorescence quenching. However, the high photon flux can also cause sample degradation, and for this reason some setups require a thermally conducting substrate (which acts as a heat sink) in order to mitigate this process.

By using Raman microspectroscopy, *in vivo* time- and space-resolved Raman spectra of microscopic regions of samples can be measured. As a result, the fluorescence of water, media, and buffers can be removed. Consequently *in vivo* time- and space-resolved Raman spectroscopy is suitable to measure cells, proteins, organs, and erythrocytes.

Raman microscopy for biological and medical specimens generally uses near-infrared (NIR) lasers (785 nm diodes and 1064 nm Nd:YAG are especially common). This reduces the risk of damaging the specimen by applying high power. However, the intensity of NIR Raman is low (owing to the ω^{-4} dependence of Raman scattering intensity), and most detectors required very long collection times. Recently, more sensitive detectors have become available, making the technique better suited to general use. Raman microscopy of inorganic specimens, such as rocks and ceramics and polymers, can use a broader range of excitation wavelengths.

See: Ellis, D.I. and Goodacre, R. (2006) Metabolic fingerprinting in disease diagnosis: biomedical applications of infrared and Raman spectroscopy, Analyst, 131, 875-885. DOI:10.1039/b602376m

History

Inelastic scattering of light is sometimes called the Raman effect, named after one of its discoverers, the Indian scientist Sir C. V. Raman (1928, together with K. S. Krishnan and independently by Grigory Landsberg and Leonid Mandelstam). Raman won the Nobel Prize in Physics in 1930 for this discovery, accomplished using filtered sunlight as a monochromatic source of photons, a colored filter as a monochromator, and a human eye as detector. For about a decade until the introduction of Fourier-transform infrared spectroscopy, this technique was used for vibrational analysis. After the invention of the laser, the technique again became widely used.

Other Types

Several variations of Raman spectroscopy have been developed. The usual purpose is to enhance the sensitivity (e.g., surface-enhanced Raman), to improve the spatial resolution (Raman microscopy), or to acquire very specific information (resonance Raman).

- **Surface Enhanced Raman Spectroscopy (SERS)** - Normally done in a silver or gold colloid or a substrate containing silver or gold. Surface plasmons of silver and gold are easily excited by the laser, and the resulting electric fields cause

other nearby molecules to become Raman active. The result is amplification of the Raman signal (by up to 10^9). This effect was originally observed by Fleishman but the prevailing explanation was explained by Van Duyne in 1977.

- **Hyper Raman** - A non-linear effect in which the vibrational modes interact with the second harmonic of the excitation beam. This requires very high power, but allows the observation of vibrational modes which are normally "silent". It frequently relies on SERS-type enhancement to boost the sensitivity.
- **Resonance Raman spectroscopy** - The excitation wavelength is matched to an electronic transition of the molecule or crystal, so that vibrational modes associated with the excited electronic state are greatly enhanced. This is useful for studying large molecules such as polypeptides, which might show hundreds of bands in "conventional" Raman spectra. It is also useful for associating normal modes with their observed frequency shifts.
- **Spontaneous Raman Spectroscopy** - Used to study the temperature dependence of the Raman spectra of molecules.
- **Optical Tweezers Raman Spectroscopy (OTRS)** - Used to study individual particles, and even biochemical processes in single cells trapped by optical tweezers.
- **Stimulated Raman Spectroscopy** - A two color pulse transfers the population from ground to a rovibrationally excited state, if the difference in energy corresponds to an allowed Raman transition. Two photon UV ionization, applied after the population transfer but before relaxation, allows the intra-molecular or inter-molecular Raman spectrum of a gas or molecular cluster (indeed, a given conformation of molecular cluster) to be collected. This is a useful molecular dynamics technique.
- **Spatially Offset Raman Spectroscopy** - The Raman scatter is collected from regions laterally offset away from the excitation laser spot, leading to significantly lower contributions from the surface layer than with traditional Raman spectroscopy. [1]

See also

- Coherent anti-Stokes Raman spectroscopy (CARS)
- Raman laser
- Resonance Raman spectroscopy

References

1. ^ P. Matousek, I.P. Clark, E.R.C. Draper, M.D. Morris, A.E. Goodship, N. Everall, M. Towrie, W.F. Finney, A.W. Parker, Subsurface Probing in Diffusely Scattering Media using Spatially Offset Raman Spectroscopy, Appl. Spectrosc. 59 (2005) 393.

External links

- Raman resource pages - Tutorial, FAQ's and application notes on various uses for Raman spectroscopy
- Raman Spectroscopy Tutorial - A detailed explanation of Raman Spectroscopy including Resonance-Enhanced Raman Scattering and Surface-Enhanced Raman Scattering.
- The Science of Spectroscopy - supported by NASA. Spectroscopy education wiki and films - introduction to light, its uses in NASA, space science, astronomy, medicine & health, environmental research, and consumer products.
- Slashdot - Discussion on using Raman spectroscopy and confocal laser scanning microscopy for 3D images of fossils embedded in solid rock
- The Science Show, ABC Radio National - Interview with Scientist on NASA funded project to build Raman Spectrometer for 2009 Mars mission: a cellular phone size device to detect almost any substance known, with commercial <USD$5000 commercial spin-off, prototyped by June 2006.
- Power Technology in depth look at Raman Spectroscopy - Applications of Raman Spectroscopy and Distributed Feedback Diodes
- Algorithms used in Spectroscopy